(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COSPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(43) International Publication Date 4 March 2004 (04.03.2004)

PCT

(10) International Publication Number WO 2004/019410 A1

(51) International Patent Classification7: 21/8246, 21/02, G11C 11/22, 11/36

H01L 27/115,

(21) International Application Number:

PCT/IB2003/003189

10 July 2003 (10.07.2003) (22) International Filing Date:

(25) Filing Language: **English**

(26) Publication Language:

English

(30) Priority Data:

02078438.5 20 August 2002 (20.08.2002) EP 03100146.4 24 January 2003 (24.01.2003)

- (71) Applicant (for all designated States except US): KONIN-KLIJKE PHILIPS ELECTRONICS N.V. [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).
- (75) Inventors/Applicants (for US only): LANKHORST, Martijn, H., R. [NL/NL]; c/o Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL)/VAN DER SLUIS, Paul [NL/NL]; c/o Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). WOLF, Ronald, M. [NL/NL]; c/o Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).

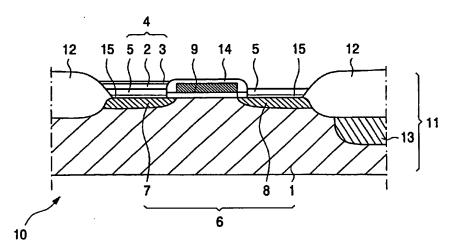
- (74) Agent: DULJVESTLJN, Adrianus, J.; Philips Intellectual Property & Standards, Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA,

[Continued on next page]

Title: FERROELECTRIC DEVICE AND METHOD OF MANUFACTURING SUCH A DEVICE



(57) Abstract: The invention relates to a ferroelectric device (10) with a body (11) comprising a substrate (1) and a ferroelectric layer (2) provided with a connection conductor (3) on a side facing away from the substrate (1), which ferroelectric layer contains an oxygen-free ferroelectric material (2) and is used to form an active electrical element (4), in particular a memory element (4). Such a device forms an attractive non-volatile memory device. In accordance with the invention, a conductive layer (5) is present between the substrate (1) and the ferroelectric layer (2), which conductive layer forms a further connection conductor (5) of the ferroelectric layer (2), and the active electrical element (4) is obtained as a result of the fact that the ferroelectric layer (2) forms a Schottky junction with at least one of the connection conductors (3, 5). In practice it has been found that such a device (10) comprises a well-performing memory element (4) that can be readily formed on a, preferably monocrystalline, silicon substrate (1). Preferably, the device (10) further comprises a field effect transistor (6), and the element (4) is preferably situated above the source or drain region (7) of the transistor (6). The active element also may function as a diode.



CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE,

DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

10

15

20

25

Ferroelectric device and method of manufacturing such a device

The invention relates to a ferroelectric device with a body comprising a substrate and a ferroelectric layer provided with a connection conductor on a side facing away from the substrate, which ferroelectric layer contains an oxygen-free ferroelectric material and is used to form an active electrical element. In case the active electrical element is a memory element, such a device constitutes a non-volatile memory and as such forms an attractive alternative to a non-volatile semiconductor memory element, partly due to the fact that it can be read very many times. The presence of an oxygen-free ferroelectric material in the dielectric layer has the important advantage that a reaction with the adjoining semiconductor material, causing the formation of an electrically insulating oxide that might adversely affect the electrical properties of the device, is precluded. The invention also relates to a method of manufacturing such a device.

A device of a type mentioned in the opening paragraph is known from United States patent specification US 5,373,176, published on 13 December 1994. In said specification a description is given of an MFS (= Metal Ferroelectric Semiconductor) structure comprising a ferroelectric layer which is provided on a CdTe semiconductor substrate and on which a gate electrode is present, which MFS structure is used to form a memory element comprising a part of the substrate and two doped regions present in the substrate. The ferroelectric layer contains an oxygen-free ferroelectric material in the form of a chalcogenide comprising ZnCdTe. The advantage of such a device is that, by virtue of epitaxial growth of the ferroelectric layer on the substrate, a high-quality interface between the (CdTe) substrate and the (ZnCdTe) ferroelectric layer can be achieved, which is necessary to obtain a properly functioning device.

In this application, chalcogenide is to be taken to mean a material that comprises a compound of at least an element, preferably a metal, and at least one of the elements S, Se and Te. Of course this compound also includes in particular mixed crystals having for example the composition $A1_xA2_{1-x}B$, where A1 comprises one or more of the elements Zn, Cd, Hg, Al, Ga, In or Tl, A2 comprises one or more of the elements Si, Ge, Sn

and Pb, and B comprises one or ore of the elements S, Se, Te, the value of x ranging between 0 and 1. Furthermore, it is to be noted that in this application, oxygen free is to be taken to mean that there is no intentional addition of oxygen into the ferroelectric material nor any intentional doping thereof with oxygen. Thus, the ferroelectric material only does contain oxygen insofar as unavoidable when using high purity materials and processing.

A drawback of the known device resides in that it requires the ferroelectric layer to be grown directly on the semiconductor substrate, which is difficult, in particular, if the substrate contains Si.

10

15

20

25

30

5

Therefore, it is an object of the present invention to provide a device which can be formed also on other substrates, such as a silicon substrate. In addition, the device should be easy to manufacture.

To achieve this, in accordance with the invention, a device of the type mentioned in the opening paragraph is characterized in that a conductive layer is situated between the substrate and the ferroelectric layer, which conductive layer forms a further connection conductor of the ferroelectric layer, and the active electrical element is formed as a result of the fact that the ferroelectric layer forms a Schottky junction with at least one of the connection conductors. The invention is based first of all on the recognition that epitaxial growth is not necessary to obtain a memory effect in a ferroelectric material. Also if the material is polycrystalline, it can be used if the crystals of the polycrystalline layer are at least predominantly ordered. The materials in question exhibit this behavior, the crystals most frequently being oriented in the direction of fastest growth. In the case of the materials considered here, this direction generally corresponds to a direction which extends substantially perpendicularly to the thickness direction of a layer grown. As a result, also a non-monocrystalline layer, which is generally true for a conductive or insulating layer, may be situated between a monocrystalline substrate and the ferroelectric layer. Even the substrate does not have to be monocrystalline. The invention is further based on the recognition that by choosing a conductive layer as an intermediate layer, if this conductive layer further serves as a connection conductor, still a memory element is formed by means of the ferroelectric layer on the proviso that at least one of the junctions of the ferroelectric layer with the connection conductor and the further connection conductor is embodied so as to be a Schottky junction. As a result, the ferroelectric layer does not have to be provided on the semiconductor substrate, which also enables a device of the desired properties to be formed using a silicon

10

15

20

25

30

substrate. Charge carriers may tunnel through the Schottky barrier associated with the Schottky junction, and the conductivity of the element may be influenced by changing the polarization, as a result of which the size of the depletion region is changed. The memory element can be switched very many times between two states.

An additional advantage of a device in accordance with the invention resides in that the manufacture thereof is very compatible with the method customarily used to manufacture silicon devices. The final process step of this method is preferably a so-termed annealing step in a hydrogen atmosphere. By virtue of the fact that the materials used, for example chalcogenide materials as defined hereinabove, do not contain oxygen, such a process step is permissible. If the ferroelectric layer contained oxygen, then hydrogen would readily influence the stoichiometry of the ferroelectric layer and hence the properties of said layer. By virtue of the fact that the dielectric layer contains an oxygen-free ferroelectric material, a reaction between the ferroelectric material and one of the adjoining metal layers, causing the formation of an electrically insulating oxide that might adversely affect the electrical properties of the device, is precluded. Finally, an important advantage resides in that said ferroelectric materials generally can be manufactured at a comparatively low temperature. This too facilitates integration within the silicon technology.

In a preferred embodiment of a device in accordance with the invention, the active electrical element is a memory element. Preferably, in a device in accordance with the invention, the body comprises — in accordance with the above explanation - a semiconductor body, and the substrate comprises a, preferably monocrystalline, semiconductor substrate. A substrate which is customary per se, such as a (100)-oriented monocrystalline silicon substrate is very suitable.

In a particularly favorable modification, a device in accordance with the invention also comprises a field effect transistor with a source region, a drain region and a gate electrode, and the further connection conductor is situated on the source region or the drain region of the field effect transistor and also serves as a connection conductor of the source region or the drain region. Such a transistor can very suitably be used as a selection means if the semiconductor device comprises a large number of memory elements, which is often desirable in practice. In addition, such a transistor can be very readily manufactured using, in particular, the technology that is based on the use of silicon as the semiconductor substrate. By virtue of the fact that the further connection conductor also serves as (one of the) connection conductor(s) of the transistor, the manufacture is comparatively simple. In addition, the device in accordance with the invention can be very compact if the source

10

15

20

25

30

region or the drain region and the memory element are situated one above the other, viewed in projection. This is an important further advantage. For example, this enables the memory element to be incorporated in a so-termed contact metal plug which is customary in many (C)MOS (= (Complementary) Metal Oxide Semiconductor) processes. These are relatively thick and frequently contain a metal such as tungsten.

In a favorable modification, the Schottky junction is formed between the further connection conductor and the ferroelectric layer and forms an ohmic contact with the source region or the drain region of the field effect transistor, while the connection conductor forms an ohmic contact with the ferroelectric layer. As a result, aluminum can be used as the connection conductor, which is quite customary in the silicon technology. As this connection conductor is situated on the outside of the device, and hence is provided in a late stage of the manufacturing process, this connection conductor is not adversely affected by the comparatively high temperatures that are frequently required in the beginning of the manufacturing process. Platinum, which is suitable to form a Schottky junction with the ferroelectric layer, can also suitably be used to form an ohmic contact with an n+-doped source region or drain region of silicon.

Materials that can suitably be used as the material for the connection conductor forming a Schottky junction with the ferroelectric layer are Pt or Au. Ag or Al can very suitably be used as the material of the connection conductor forming an ohmic contact with the ferroelectric layer.

Favorable results are achieved by using a ferroelectric layer comprising as the oxygen-free ferroelectric material a chalcogenide such as Zn_xCd_{1-x}S, preferably Zn_xCd_{1-x}S having a Zn content of x ranging between 0.3 and 0.5. Very usable results have also been obtained by using Cu₂S as the oxygen-free ferroelectric material. An important additional advantage of such a material is that it does not contain toxic constituents. Thus, in such a case there is no or substantially no burden on the environment when the device is disposed of for example after its useful life. Another consequence of this is that in particular the safety of the manufacturing environment wherein a device in accordance with the invention is manufactured is improved. Starting materials such as Cd are banned more and more from the manufacturing environment. In the case of Cu₂S use can advantageously be made of Cu and W for the connection conductors. These too are materials that are increasingly permitted and that are applied in the (silicon) semiconductor technology.

Preferably the doping concentration of the oxygen-free ferroelectric material is chosen to be so high that an ohmic contact between the connection conductor or the further

10

15

20

25

30

. C...... a a

connection conductor and the ferroelectric layer is formed, and that, during operation, the electric field in the ferroelectric layer in the conducting state is sufficiently high to switch off the memory element.

5

Preferably, a device in accordance with the invention comprises a matrix of N x M memory elements, where N and M are natural numbers and each memory element is connected on both sides to an electric connection. A memory having a large capacity may thus have been formed. Preferably, each memory element is coupled to an associated field effect transistor with a source region, a drain region and a gate electrode, and the device is provided with N first conductor tracks and M second conductor tracks and with a ground connection, and each memory element is connected via the connection conductor to one of the N first conductor tracks and via the further connection conductor to the source region or drain region of the field effect transistor whose drain region or source region is connected to the ground connection, and the gate electrode of the field effect transistor is connected to one of the M second conductor tracks. This construction enables the memory elements to be read while the number of necessary conductor tracks is limited.

It is to be noted that a device according to the invention may also form a diode like device with important advantages. The advantages of these novel diodes compared with existing diodes are: a low operating voltage for the same forward-reverse current ratio, a high current density in the forward direction and thus a low area for the same forward current and the fact that they do not require a single-crystal substrate. In one embodiment, the device is used as a diode outside a voltage range where a memory effect related to the ferroelectric behavior occurs. This voltage range is shown in Fig. 2 between points A and B.

A method of manufacturing a ferroelectric device in accordance with the invention, wherein a body is formed having a substrate, and the device is provided with a ferroelectric layer which is provided with a connection conductor, an oxygen-free ferroelectric material being used as the material for the ferroelectric layer, and said ferroelectric layer being used to form an active electrical element, is characterized in that a conductive layer is provided between the substrate and the ferroelectric layer, which conductive layer is used to form a further connection conductor of the ferroelectric layer, and the active electrical element is formed by forming a Schottky junction between the ferroelectric layer and at least one of the connection conductors. In this manner a ferroelectric device having the above-discussed advantages is obtained in a simple manner. In a preferred embodiment, the active electrical element is formed as a memory element. Preferably, the body takes the form of a semiconductor body and a, preferably monocrystalline,

10

15

20

25

30



semiconductor substrate is used as the substrate. Preferably, a field effect transistor with a source region, a drain region and a gate electrode is formed in the semiconductor body, and the further connection conductor is provided on the source region or the drain region of the field effect transistor and formed to a connection conductor of the source region or the drain region.

In a favorable modification, the ferroelectric layer is formed by converting part of a conductive layer to the ferroelectric material, one of the connection conductors being formed by the remaining part of the conductive layer. As a result, the method is simplified and good contact between the metal and the oxygen-free ferroelectric material is obtained. A Cu layer can thus be partly converted to Cu₂S.

In a favorable modification, the Schottky junction is formed between the further connection conductor and the ferroelectric layer, which further connection conductor also serves as the connection conductor of the source region or the drain region, while an ohmic contact is formed between the connection conductor and the ferroelectric layer. Preferably a matrix of N x M memory elements is formed, where N and M are natural numbers, and each memory element is provided on both sides with an electric connection. Preferably, each memory element is coupled to a field effect transistor formed in the device and associated with the memory element, which field effect transistor has a source region, a drain region and a gate electrode, and the device is provided with N first conductor tracks and M second conductor tracks and with a ground connection, and each memory element is connected via the connection conductor to one of the N first conductor tracks and via the further connection conductor to the source region or the drain region of the associated field effect transistor whose drain region or source region is coupled to the ground connection, and the gate electrode of the field effect transistor is coupled to one of the M second conductor tracks.

These and other aspects of the invention are apparent from and will be elucidated with reference to the embodiment(s) described hereinafter.

In the drawings:

Fig. 1 is a diagrammatic cross-sectional view, at right angles to the thickness direction, of a ferroelectric device in accordance with the invention,

Fig. 2 shows the current-voltage characteristic of the memory element of the device shown in Fig. 1, and

20

25

30



Fig. 3 diagrammatically shows the circuit of the device shown in Fig. 1, and Fig. 4 shows the current-voltage characteristic of a modification of the memory element of the device shown in Fig. 1.

The Figures are not drawn to scale and some dimensions, such as dimensions in the thickness direction, are exaggerated for clarity. In the Figures like reference numerals refer to like areas or parts whenever possible.

Fig. 1 is a diagrammatic cross-sectional view, at right angles to the thickness

direction, of a ferroelectric device 10 in accordance with the invention. Said device 10

comprises a semiconductor body 11 having a semiconductor substrate 1. This semiconductor

device further comprises a ferroelectric layer 2 that is provided with a connection conductor 3

on a side facing away from the substrate 1. By means thereof, in this case a memory element

4 is formed, and the ferroelectric 2 comprises an oxygen-free ferroelectric material, here a

chalcogenide.

In accordance with the invention, a conductive layer 5, preferably a metal layer 5, is situated between the semiconductor substrate 1 and the ferroelectric layer 2, which conductive layer forms a further connection conductor 5 of the ferroelectric layer 2, and the memory element 4 is obtained as a result of the fact that the ferroelectric layer 2 forms a Schottky junction with at least one of the connection conductors 3, 5. Such a device 10 can be formed very readily on a semiconductor substrate 1 of silicon and still have a memory element 4 with excellent properties, as will be explained in greater detail hereinafter. An important additional advantage of a device 10 in accordance with the invention resides in that the manufacture thereof is highly compatible with the method customarily used to manufacture silicon devices. The final process step of this method advantageously is an annealing step in a hydrogen-containing atmosphere. Such an annealing step is permissible by virtue of the fact that the ferroelectric material used does not contain oxygen. If the ferroelectric layer 2 were to contain oxygen, hydrogen would readily influence the stoichiometry of the ferroelectric layer and hence the properties of said layer 2.

In this example, the device 10 also comprises a field effect transistor 6 with a source region 7, a drain region 8 and a gate electrode 9, and the further connection conductor 5 is situated on the source region or the drain region, in this case the source region 7 of the transistor 6, and is also used as a connection conductor 5 of the source or drain region 7, 8. In this example, viewed in projection, the memory element 4 is situated within the source region

10

15

20

25

30



or the drain region; in this case within the drain region 7. As a result, the device 10 is compact and can be manufactured relatively readily. The presence of a field effect transistor 6 is very advantageous if, as in this example, the device 10 comprises a large number of memory elements 4 and each memory element 4 is coupled to a field effect transistor as shown in Fig. 1. The device 10 of this example thus forms a semiconductor memory with a large number of memory elements 4, only one of which is shown in Fig. 1.

In the device 10 of this example, the Schottky junction is formed between the further connection conductor 5, here a platinum layer 5, and the ferroelectric layer 2, here a Zn_xCd_{1-x}S layer 2 having a Zn content x of approximately 40 at.%. Via a thin, here 10 nm, Ti layer 15 which serves as a barrier, the platinum 5 forms an ohmic contact with the source region 7 of transistor 6. The connection conductor 3, here containing Ag, forms an ohmic contact with the ferroelectric layer 2. The thicknesses of the layers are 100 nm for the Zn_xCd_{1-x}S layer 2, 50 nm for the Pt layer 5 and 50 nm for the Ag layer 3. The lateral dimensions of the memory element 4 are, in this example, 1 µm x 1 µm. A suitable thickness for the Zn_xCd_{1-x}S layer ranges between 25 nm and 500 nm. The doping concentration of the Zn_xCd_{1-x}S layer 2 is chosen to be such that, on the one hand, it is high enough to enable an ohmic contact to be established between the further connection conductor 5 and the ferroelectric layer 2. On the other hand, the doping concentration should not be chosen to be so high that, during operation, the electric field in the ferroelectric layer 2 in the conducting state is not high enough to switch off the memory element. The operation of the device 10 and, in particular, of the memory element 4 will be illustrated hereinafter with reference to Fig. 2.

Fig. 2 shows the current-voltage characteristic of the memory element 4 of the device 10 of this example. At the origin, where the element 4 is in a state of low impedance, the current I rises with increasing voltage V in accordance with curve 21. At point A, where the voltage is approximately +0.3 volt, the Zn_xCd_{1-x}S layer 2 changes its polarization and the element 4 switches to the high-impedance state. A further increase of the voltage V has no further effect. If the voltage V is reduced, the element V remains in the high-impedance state shown in curve 22 until the reverse switching voltage is reached at approximately -0.1 volt, indicated in the Figure by means of point B. From that moment the element is (again) in the low-impedance state shown in curve 21. A further reduction of the voltage V to -0.4 volt has no further effect. The operation of the device 10 will normally be as follows: bring the element 4 to the high-impedance state ("0") by means of a short voltage pulse of +0.4 V, and to the low-impedance state ("1") by means of a short voltage pulse. Read the impedance of

10

15

20

25

30

the element 4 at a low voltage V, such as a voltage V whose absolute value is smaller than approximately 0.1 V. As mentioned hereinabove, the device 10 comprises a large number of memory elements 4, four of which are shown in Fig. 3.

Fig. 3 diagrammatically shows the circuit of the device 10 of this example. The device 10 comprises a number, for example 100, of first conductor tracks 20, two of which are shown in Fig. 3, and a number, here also 100, of second conductor tracks 30, two of which are shown in Fig. 3. Each element 4 is connected via a connection conductor 3 to one of the first conductor tracks 20 and via the further connection conductor 5 to the source region 7 of the transistor 6. The drain region 8 of the transistor 6 is connected to a ground connection 40, while the gate electrode 9 of the transistor 6 is connected to one of the second conductor tracks 30. Thus, by applying a voltage to the gate electrode 9, it is possible to select, via the transistor 6, the associated element 4 to adjust and/or read the impedance state.

The device 10 of this example is manufactured in the following manner by means of a method in accordance with the invention. There is started from (see Fig. 1) a (100) silicon substrate 1 with a p-type doping in a low doping concentration. In said substrate there is formed, in a manner which is known per se using customary processes, an N-MOS transistor 6 having n-type source regions 7 and drain regions 8 surrounded by LOCOS (= LOCal Oxidation of Silicon) regions 12. Below these, on the side of the drain region 8, a part of an n-type region 13 is visible in this case, wherein a complementary P-MOS transistor, not shown, is formed. The gate electrode 9 is made of n-type polycrystalline silicon and is surrounded by isolating layers 14 containing silicon dioxide and/or silicon nitride. A titanium layer 15 and a platinum layer 5 are applied to the source region 7 and the drain region 8 by means of, for example, sputtering and form an ohmic contact with said regions. Locally, here at the location of the source region 7, a Zn_xCd_{1-x}S layer is provided thereon by means of sputtering. This technique is particularly suitable for applying Zn_xCd_{1-x}S of a stoichiometric composition, here containing 40 at.% Cd. At the location of the source region 7, the patterned Zn_xCD_{1-x}S layer 2 is provided with a silver layer 3 forming an ohmic contact with the Zn_xCd_{1-x}S layer 2. The conductive layers 3, 5 are separated from the first and the second conductor tracks 20, 30 by means of a silicon dioxide layer, not shown, which is provided, for example, by means of CVD (= Chemical Vapor Deposition). The same applies to the mutual insulation of the first and the second conductor tracks 20, 30 which, as shown in Fig. 3, are connected to each transistor 6 and each memory element 4. The manufacturing process is completed by providing a silicon nitride protective layer, not shown, after which the device 10 is annealed by means of an annealing step in a hydrogen-containing atmosphere.

10

15

20

25

30

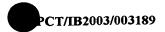


Fig. 4 shows the current-voltage characteristic of another modification of the memory element 4 of the device 10 of the above-described example. In this example the memory element 4 comprises a ferroelectric layer 2 containing Cu₂S as the oxygen-free ferroelectric material. The connection conductor 3 and the further connection conductor 5 contain, respectively, Cu and W in this example. A very important advantage of the device of this modification is that the elements that it contains are not toxic or at least not appreciably toxic. As a result, the burden on the environment when the device is disposed of after its useful life as well as its permissibility in a manufacturing environment are substantially improved. The image shown in Fig.4 corresponds substantially to that shown in Fig.2. For the operation of this modification of the device in accordance with the invention reference is made to the description pertinent to Fig. 2. the safety of the manufacturing environment wherein a device in accordance with the invention is manufactured is improved.

In the device shown in Fig. 4, the Cu₂S is formed preferably, like in this modification, by partly converting a Cu layer to Cu₂S. In this case, such a conversion is carried out by treating a Cu layer with an aqueous solution of $K2S_x$, where x > 1. This has the advantage that, simultaneously with the oxygen-free ferroelectric layer, one of the two connection conductors is formed by, in this case, the remaining Cu layer.

Other modifications of devices in accordance with the invention can be formed in a simple manner by choosing different oxygen-free ferroelectric materials for the ferroelectric layer 2, such as, in particular, ferroelectric materials within the groups of compounds referred to as picnides, chalcogenides and halogenides, i.e. compounds of one or more elements, of which one or more elements are from main group V, VI (with the exception of oxygen) and VII of the periodic system of elements, and mixed crystals thereof. Theoretically suitable oxygen-free ferroelectric materials are, for example, Al₅C₃N, Al₇C₃N₃, Sb_2S_3 , Bi_2S_3 , Bi_2S , $Bi_0.5Sb_{1.5}S_2$, $TaInS_2$, $TaNbSe_2$, $TlSbSe_2$, $Bi_0.5Sb_{1.5}S_2$, $Ga_xGe_{1-x}Te$, where 0 < x < 1, SbSI, Cs₃BiCl₆, AMX₃, where A = Cs or Rb and M = Ca, Cr, Ti, V or Cu and X = F, Cl, Br or I, BaMF₄, where M = Mg, Mn, Fe, Co, Ni, Cu or Zn, SrAlF₅, K₂MF₆, where M =Mn, Cr, Ti or Pd, $A_3M_3F_{19}$, where A = Sr, Ba or Pb and M = Al, Ti, V, Cr, Fe or Ga. Of these oxygen-free ferroelectric materials, Bi₂S₃ and SbSI have a comparatively low Curie temperature, which limits the practical use of these materials. The same applies to the compounds of thallium, due to the toxicity of these compounds. The practical use of the compounds listed above, starting from Cs₃BiCl₆, may be limited by too high an ionic conductance, which may cause the data stored to be lost.

10

15

20

25

An example of a ferroelectric device according to the invention in which the active element is a diode-like device was realized with a ferroelectric layer comprising ZnCdS between a platinum layer and a silver layer. Especially low (forward) voltages are obtained when the ferroelectric semiconductor layer is thin an/or has a low coercive field and/or a Curie temperature which is close to the operating temperature. Typical values for the coercive field (kV/cm), the film thickness (nm) and switch voltage (V) are: 20 kV/cm, 30 nm and 0,06 V respectively, or 30 kV/cm, 30 nm and 0,06 V respectively.

The invention is not limited to the above-described example and, within the scope of the invention, many variations and modifications are possible to those skilled in the art. For example, devices having a different geometry and/or different dimensions can be manufactured. It is also possible to employ different materials for, in particular, the connection conductors, such as hafnium carbide or other binary materials.

What has been observed hereinabove regarding the device also applies to the manufacture thereof. As well as the above-mentioned techniques for applying the ferroelectric layer, also MBE (= Molecular Beam Epitaxy), (MO)VPE (= (Metal Organic) Vapor Phase Epitaxy or CVD (= Chemical Vapor Deposition) or PLD (Pulsed Laser Deposition) can be used.

It is further noted that the device may comprise further active and passive semiconductor elements such as diodes and/or transistors and resistors and/or capacitance's. This enables additional circuits to be advantageously formed which are capable of fulfilling additional functions.

Finally, it is noted again that a device in accordance with the invention may also advantageously comprise a substrate other than a monocrystalline substrate. Also a substrate of a conductor, such as a metal, or of an insulator, such as glass, ceramic or synthetic resin can be advantageously applied.

CLAIMS:

5

15

20

25

- 1. A ferroelectric device (10) with a body (11) comprising a substrate (1) and a ferroelectric layer (2) provided with a connection conductor (3) on a side facing away from the substrate (1), which ferroelectric layer contains an oxygen-free ferroelectric material and is used to form an active electrical element (4), characterized in that a conductive layer (5) is situated between the substrate (1) and the ferroelectric layer (2), which conductive layer forms a further connection conductor (5) of the ferroelectric layer (2), and the active electrical element (4) is formed as a result of the fact that the ferroelectric layer (2) forms a Schottky junction with at least one of the connection conductors (3, 5).
- 2. A ferroelectric device (10) as claimed in claim 1, characterized in that the active electrical element (4) is a memory element (4).
 - 3. A ferroelectric device (10) as claimed in claim 2, characterized in that the body (11) comprises a semiconductor body (11), and the substrate (1) comprises a, preferably monocrystalline, semiconductor substrate (1).
 - 4. A ferroelectric device (10) as claimed in claim 3, characterized in that the semiconductor body (11) comprises a field effect transistor (6) with a source region (7), a drain region (8) and a gate electrode (9), and the further connection conductor (5) is situated on the source or drain region (7) of the field effect transistor and also serves as a connection conductor (5) of the source region or drain region (8).
 - 5. A ferroelectric device (10) as claimed in claim 4, characterized in that the memory element (4) and the source or drain region (7) show an overlap, viewed in projection.
 - 6. A ferroelectric device (10) as claimed in claim 4 or 5, characterized in that the Schottky junction is formed between the further connection conductor (5) and the ferroelectric layer (2), and the further connection conductor (5) forms an ohmic contact with

20

25

the source or drain region (7) of the field effect transistor (6), while the connection conductor (3) forms an ohmic contact with the ferroelectric layer (2).

- 7. A ferroelectric device (10) as claimed in any one of the preceding claims, 5 characterized in that a chalcogenide is selected as the ferroelectric material.
 - 8. A ferroelectric device (10) as claimed in claim 7, characterized in that the selected chalcogenide is $Zn_xCd_{1-x}S$, preferably $Zn_xCd_{1-x}S$ having a Zn content of x in the range between 0.3 and 0.5.
 - 9. A ferroelectric device (10) as claimed in claim 8, characterized in that Pt or Au is selected as the material for one connection conductor (3) and Ag or Al is selected as the material for the other connection conductor (5).
- 15 10. A ferroelectric device (10) as claimed in claim 7, characterized in that Cu₂S is selected as the chalcogenide.
 - 11. A ferroelectric device (10) as claimed in claim 10, characterized in that Cu is selected as the material for one connection conductor (3) and W is selected as the material for the other connection conductor (5).
 - 12. A ferroelectric device (10) as claimed in claim 2, 3, 4, 5 or 6, characterized in that the doping concentration of the oxygen-free ferroelectric material is so high that an ohmic contact between the connection conductor (3) or the further connection conductor (5) and the ferroelectric layer (2) is formed, and that, during operation, the electric field in the ferroelectric layer (2) in the conducting state is sufficiently high to switch off the memory element (4).
- 13. A ferroelectric device (10) as claimed in Claim 12, characterized in that said ferroelectric device comprises a matrix of N x M memory elements (4), where N and M are natural numbers and each memory element (4) is connected on both sides to an electric connection (20, 30).

A ferroelectric device (10) as claimed in claim 13, characterized in that each memory element (4) is coupled to an associated field effect transistor (6) with a source region (7), a drain region (8) and a gate electrode (9), and the device is provided with N first conductor tracks (20), M second conductor tracks (30) and with a ground connection (40), and each memory element (4) is connected via the connection conductor (3) to one of the N first conductor tracks and via the further connection conductor (5) to the source or drain region (7) of the field effect transistor (6), of which the other drain or source region (8) is connected to the ground connection (40), while the gate electrode (9) of the field effect transistor (6) is connected to one of the M second conductor tracks (30).

10

30

5

- 15. A ferroelectric device (10) as claimed in claim 1, characterized in that the active electrical element (4) is a diode.
- 16. A method of manufacturing a ferroelectric device (10) as claimed in any one
 15 of the preceding claims, wherein a body (11) is formed that comprises a substrate (1), and the
 device (10) is provided with a ferroelectric layer (2) provided with a connection conductor
 (3) on a side facing away from the substrate (1), an oxygen-free ferroelectric material being
 selected as the material for the ferroelectric layer which is used to form an active electrical
 element (4), characterized in that a conductive layer is provided between the substrate (1) and
 20 the ferroelectric layer (2), which conductive layer forms a further connection conductor of the
 ferroelectric layer (2), and the memory element (4) is obtained by forming a Schottky
 junction between the ferroelectric layer (2) and at least one of the connection conductors (3,
 5).
- 25 17. A method according to claim 16, characterized in that the active electrical element (4) is formed as a memory element (4).
 - 18. A method as claimed in claim 17, characterized in that the body (11) is formed so as to be a semiconductor body (11), and a semiconductor substrate (1) is selected as the substrate (1).
 - 19. A method as claimed in claim 17, characterized in that in the semiconductor body (11) there is formed a field effect transistor (6) with a source region (7), a drain region (8) and a gate electrode (9), and the further connection conductor (5) is provided on the



source or drain region (7) of the field effect transistor (6) and is formed so as to be a connection conductor (5) of the source region or drain region (7).

- A method as claimed in claim 17, 18 or 19, characterized in that the Schottky junction is formed between the further connection conductor (5) and the ferroelectric layer (2), and an ohmic contact is formed between the connection conductor (3) and the ferroelectric layer (2) as well as between the further connection conductor (5) and the source or drain region (7) of the field effect transistor (6).
- 10 21. A method as claimed in claim 17, 18, 19 or 20, characterized in that the ferroelectric layer (2) is formed by converting part of a conductive layer to the ferroelectric material, one of the connection conductors (3, 5) being formed by the remaining part of the conductive layer.
- 15 22. A method as claimed in any one of claims 17 through 21, characterized in that a matrix of N x M memory elements (4) is formed, where N and M are natural numbers and each memory element (4) is provided on both sides with an electric connection.
- 23. A method as claimed in claim 22, characterized in that each memory element
 20 (4) is coupled to a field effect transistor (6) formed in the device (10) and associated with
 said memory element (4), which field effect transistor comprises a source region (7), a drain
 region (8) and a gate electrode (9), and the device (10) is provided with N first conductor
 tracks (20), M second conductor tracks (30) and with a ground connection (40), and each
 memory element (4) is connected via the connection conductor (3) to one of the N first
 25 conductor tracks (20) and via the further connection conductor (5) to the source or drain
 region (7) of the associated field effect transistor (6), of which the other drain or source
 region (8) is connected to the ground connection (40), while the gate electrode (9) is
 connected to one of the M second conductor tracks (30).
- 30 24. Method of operating a ferroelectric device (10) as claimed in claim 15, characterized in that the ferroelectric device (10) is operated outside the voltage region where the ferroelectric memory effect occurs.

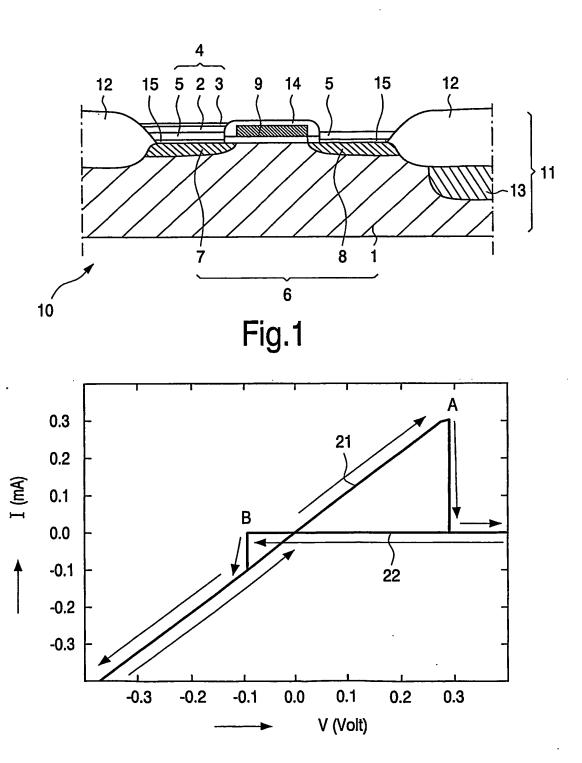
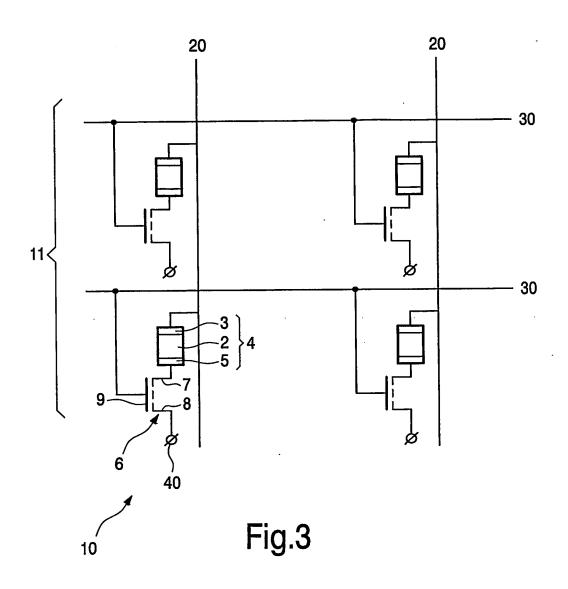


Fig.2



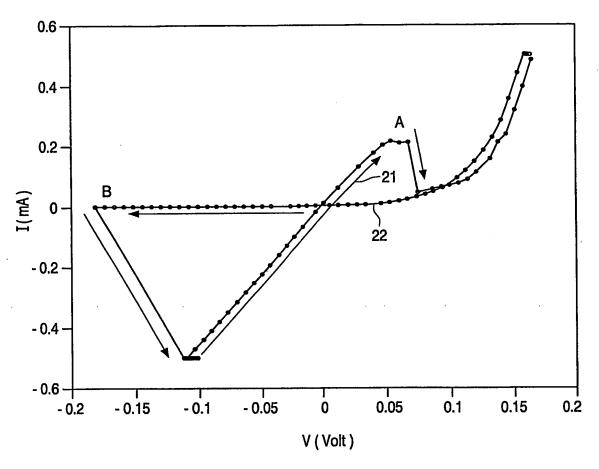


FIG. 4

INTERNATIONAL ARCH REPORT

PCT/IB 03189

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 H01L27/115 H01L21/8246 H01L21/02 G11C11/22 G11C11/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01L G11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, INSPEC

C. DOCUM	ENTS CONSIDERED TO BE RELEVANT			
Category °	Citation of document, with indication, where appropriate, of th	e relevant passages	Relevant to daim No.	
Υ	EP 0 660 412 A (PHILIPS ELECTR 28 June 1995 (1995-06-28) the whole document	ONICS NV)	1-24	
Υ	JP 11 286772 A (JAPAN SCIENCE TECHNOLOGY CORP) 19 October 1999 (1999-10-19) the whole document & PATENT ABSTRACTS OF JAPAN vol. 2000, no. 01, 31 January 2000 (2000-01-31) & JP 11 286772 A (JAPAN SCIENCE TECHNOLOGY CORP), 19 October 1999 (1999-10-19) abstract		1-24	
X Fur	ther documents are listed in the continuation of box C.	Patent family members are listed	I in annex.	
° Special c	ategories of died documents :	"T" later document published after the Int	ernational filing date	
cons	nent defining the general state of the art which is not idered to be of particular relevance	or priority date and not in conflict with cited to understand the principle or the invention	the application but	
"E" earlier filing	document but published on or after the international date	"X" document of particular relevance; the cannot be considered novel or canno	claimed invention	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or		involve an inventive step when the description of particular relevance; the cannot be considered to involve an indocument is combined with one or ments, such combination being obvi	ocument is taken alone ctaimed invention nventive step when the tore other such docu-	
	r means nent published prior to the international filing date but	in the art.	•	

*8' document published prior to the international filling date but later than the priority date claimed

*8' document member of the same patent family

Date of the actual completion of the international search

19 November 2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016

Albrecht, C



PCT/I /03189

Continu	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	PCT/I 3/03189
ory °		Relevant to claim No.
	WO 95 08187 A (RADIANT TECHNOLOGIES INC) 23 March 1995 (1995-03-23) the whole document	1-24
	EP 0 936 678 A (SIEMENS AG) 18 August 1999 (1999-08-18) the whole document	1-14

INTERNATIONAL SEARCH REPORT

PCT/I 3/03189

Patent do			Publication date		Patent family member(s)		Publication date
EP 0660	0412	A	28-06-1995	BE CN EP JP US	1007902 1108816 0660412 7202139 5512773	A A1 A	14-11-1995 20-09-1995 28-06-1995 04-08-1995 30-04-1996
JP 1128	B6772	Α	19-10-1999	NONE			
WO 9508	8187	Α	23-03-1995	US AU WO	5440173 7478494 9508187	A	08-08-1995 03-04-1995 23-03-1995
EP 093	6678	Α	18-08-1999	EP JP TW US	0936678 11274417 417279 6359296	A B	18-08-1999 08-10-1999 01-01-2001 19-03-2002